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IGB 1532

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Assistant Commissioner for Patents
Washington, D.C. 20231

SUBMISSION OF PRIORITY DOCUMENT UNDER 37 C.F.R. §1.55(a)

Sir:

Applicants filed the present application claiming the benefit, under the conditions specified in 35 U.S.C. §119, of the filing date of prior Great Britain Patent application 9927167.8 filed November 18, 1999.

Applicant herein submits a certified copy of the priority application pusuant to 37 C.F.R. § 1.55(a).

Respectfully submitted,
Attorney for Applicants

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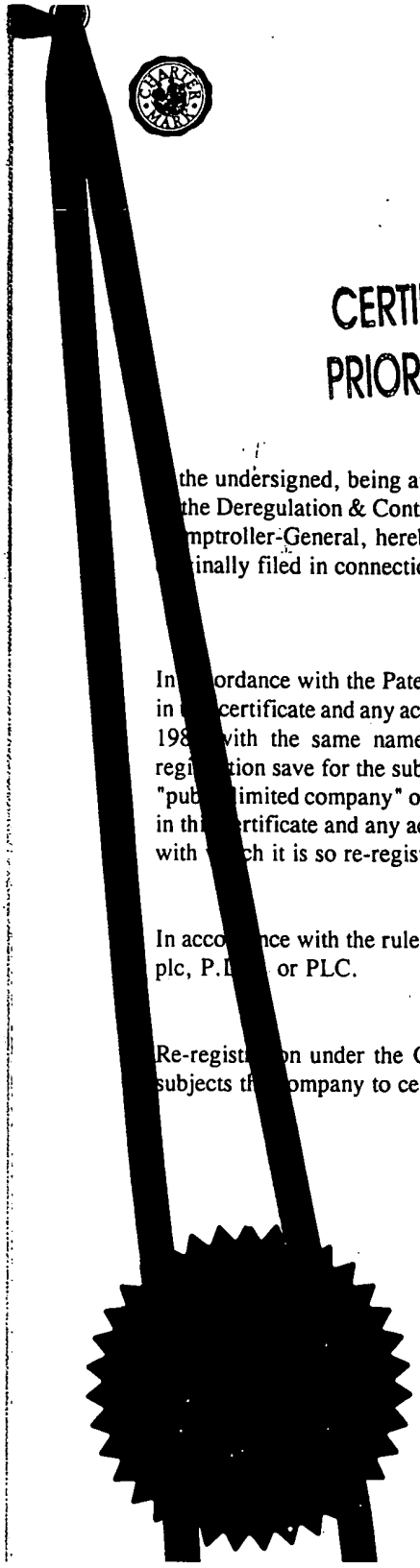

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IGB 1532

**New Patent Application**

| | |
|---|---|
| Applicant: | ILFORD Imaging UK Limited<br>and<br>ILFORD Imaging Switzerland GmbH |
| Entitled: | Printing Process |
| Case No: | IGB 1532 |

This invention relates to a recording medium and to a method for the treatment of images produced therewith.

## BACKGROUND OF THE INVENTION

This invention relates to the treatment of images prepared using so-called aqueous inks, that is to say inks in which water comprises the major component of the liquid phase. There is increasing interest in the use of aqueous inks for environmental and safety reasons.

Printing media suitable for use with aqueous inks are well known. Commonly these employ at least one ink receiving layer coated on a suitable substrate. The purpose of the receiving layer is to take up the ink rapidly and improve image quality. One problem with images produced using aqueous inks is that they can be insufficiently robust to handling, and that the image or the receiving layer on which it is printed is sensitive to rubbing and scratching. In addition the printed image frequently becomes more sensitive to handling and damage under damp conditions, and can sometimes be washed completely away.

Several methods of overcoming the poor robustness of images produced using aqueous inks are known. For instance various additional coatings and treatments for ink receiving layers have been proposed, such as lacquers or

varnishes which have to be applied after printing the image, thus requiring additional equipment. For instance our pending British Patent Application number 9810649.5 provides a method for increasing the rub resistance of an image by coating or over-printing the image with an aqueous solution of a styrene acrylate polymer.

Another method of improving the robustness of printed images is to laminate or encapsulate them, and this is particularly common when they are intended for external display. By lamination is meant the combination of a printed image with a transparent overlay, this combination usually being accomplished with an adhesive activated by heat, pressure, or both. The overlay acts as a physical protection for the image and completely seals it from ingress of water. By encapsulation is meant the combination of a printed image layer between two laminating sheets, that on the image surface being transparent, the combination being accomplished with an adhesive activated by heat, pressure, or both. Encapsulation is most effective if the laminating sheets extend beyond the printed image and are bonded to each other at the extremities, thus preventing ingress of water through exposed edges of the image.

However lamination and encapsulation are both expensive because additional materials are required together with additional handling and equipment, and

there is considerable interest in finding a cheaper and simpler method of increasing the robustness of images produced using aqueous inks.

As an alternative to lamination or overprinting, Japanese Patent Applications 59/222381, 07/237348, 08/02090, and 09/104164 and European Patent Applications 0 858 905 and 0 858 906 disclose a heat seal method of protecting an ink jet image wherein the receiving system comprises two layers coated on a suitable base. The lower layer is an ink receiving layer which is absorbent to the ink, whereas the upper layer comprises a film forming polymer in a binder. After printing the upper layer may be sealed by heating to form a robust barrier to protect the image in the lower layer. This is similar to laminating the image, but does not require the additional expensive lamination sheet.

However this heat seal method needs to achieve high temperatures to seal the image (up to 170° being given in the Examples of EP 0 858 906 A) and also requires a relatively complicated and expensive receiving sheet. There is thus still a need for an imaging material and method which will provide images resistant to washing and handling when printed using aqueous inks without lamination. We have found a material and method which achieves these objectives.

## SUMMARY OF THE INVENTION

According to the present invention there is provided a printing method which comprises the steps of:-

1) Printing on to a receiving material which comprises on a suitable substrate at least one ink receiving layer which comprises a particulate polymer which is characterised by a film forming temperature of between 100° and 120° together with at least one hydrophilic binder, and

2) Subsequently heating and applying pressure to the printed image to fuse the polymer.

The method and materials of the invention are much simpler than previously known heat sealing methods for printed images because the receiving layer may consist of only a single layer rather than the minimum of two known previously, and is thus considerably simpler and cheaper to manufacture. The receiving layers of the invention provide bright images after printing and fusing which show a high level of scratch and rub resistance even when wet.

## DETAILED DESCRIPTION OF THE INVENTION

Suitable substrates to carry the layers of the invention include any of those commonly used for printing and imaging media, for example paper, high

wet-strength paper, tracing paper, heavyweight paper, card, board, treated paper such as resin or polyethylene coated paper, transparency materials, synthetic papers, canvas, cloth, fabric, metals such as aluminium, and polymeric substrates such as cellulose acetates, poly(ethylene), poly(propylene), poly (vinyl chloride), and polyesters including poly (ethylene terephthalate) and poly (ethylene naphthalate).

Suitable hydrophilic binders include poly (vinyl alcohol), copolymers of poly (vinyl alcohol), carbohydrates such as tragacanth gum, casein, or starch, modified carbohydrates such as hydroxyethyl cellulose or carboxymethyl cellulose, polyacrylates, poly (vinyl pyrrolidone), poly(ethylene imine), gelatin, and mixtures of such binders. A particularly suitable hydrophilic binder is poly (vinyl alcohol). It is to be understood that commercial samples of poly (vinyl alcohol) are normally prepared by hydrolysis of poly (vinyl acetate), and that this hydrolysis does not always go to completion. Thus a preferred hydrophilic binder is poly (vinyl alcohol) which has a degree of hydrolysis of at least 90%, and a particularly preferred binder is poly (vinyl alcohol) which has a degree of hydrolysis of about 99%. This is hereinafter referred to as 99%PVA.

Suitable polymers for the particulate polymer include low density polyethylene and copolymers of ethylene with other ethylenically unsaturated monomers, such as acrylate monomers. A suitable particle size for the

particulate polymer is between about 1 μm and about 50 μm, with a particle size between about 5 μm and about 20 μm being preferable. A particularly suitable particulate polymer comprises low density polyethylene spherical beads having an average diameter of about 12 μm. Another particularly suitable particulate polymer comprises spherical beads of a 7% acrylic acid/ polyethylene copolymer having an average diameter of about 10 μm. Another suitable particulate polymer comprises polyethylene beads of random shape and a particle size of about 25 μm. These polymers have crystalline melting points of 105-107°C.

A suitable coating weight for the receiving layer is from about 5 to about 50 $gm^{-2}$. A preferred coating weight for the receiving layer is from about 20 to about 40 $gm^{-2}$. The ratio of the coating weight of the particulate polymer to that of the hydrophilic binder may be from about 20:1 to about 1:1, but preferably is between about 10:1 and about 5:1.

The receiving layer may advantageously also comprise additives which are commonly added to ink receiving layers such as surfactants to improve coating quality, cross linking agents, optical brightening agents, inorganic pigments or fillers such as chalk, silica, alumina, kaolin and the like, light stabilisers, biocides, and dye fixatives such as the polymers provided by United States Patents 5 342 688, 5 589 269, and 5 712 027. Suitable cross linking agents for the preferred poly (vinyl alcohol) binders of the invention include aldehydes

such as glyoxal, boric acid, poly ethylene imines, and divalent metallic cations.

According to a preferred aspect of this invention, the printed image is heated by passing through a laminator. By laminator is meant a device which is normally used for the lamination of printed images which comprises a means of heating and pressing together the image and the laminating sheet thus causing the two to adhere, commonly by passing them through heated rollers. This aspect is particularly preferable because many printing and processing houses already possess and use laminators which can be applied to the materials of this invention. However the advantage of this invention is that the additional expensive lamination sheet is unnecessary.

According to another aspect of the invention, the printed image is heated by passing through a laminator in conjunction with a second, inert sheet which is held against the image protective layer of the material. The inert sheet does not adhere to the material, but protects it from the rollers of the laminator. Moreover the use of a smooth inert sheet will impart a high gloss or other desired appearance to the final image. Alternatively a suitable choice of the inert sheet may be used to produce a pattern such as a security symbol after contacting with the image. The inert sheet may then be recycled almost indefinitely.

The method and materials of the invention are particularly suited to the treatment of images produced using ink jet printers, as aqueous inks are commonly used in such printers, particularly those designed for use in the home or office. Ink jet printing is a non impact printing method that in response to a digital signal produces droplets of ink that are deposited on a substrate to produce an image. Ink jet printing has found broad application in recent years. Any convenient ink jet printer may be used, for example a continuous printer or a piezoelectric or thermal drop-on-demand printer.

The invention may also be used with other printing methods employing aqueous inks such as flexographic printing, with pen type plotters, or with aqueous marker pens and the like. Suitable colorants for the inks include dyes or pigments. Preferred inks for the invention are pigmented inks.

The materials and method of this invention are suitable for many uses where robustness of an ink jet image is important, such as posters, banners, displays, labels, and the like. The method of this invention is also particularly suitable for use with a wide variety of packaging materials, e.g a heavy weight paper, card, or board.

The materials and method of this invention are also particularly suitable as a security printing system, and this aspect of the invention is especially preferred. After the material has been sealed by heating it is no longer

receptive to inks, and is thus difficult to alter and offers high levels of protection from fraud and forgery. In an additional aspect of the invention when it is used as a security printing system, a suitable mark or pattern such as, for example, a holographic pattern may be embossed on or transferred to the image at the heating stage. This pattern may be carried on the inert sheet used in contact with the image during the heating stage, or may be carried on a roller or stamp used in contact with the image at the heating stage.

Various ink receiving materials which comprise a combination of a particulate polymer and a hydrophobic binder are already known. For instance United States Patent 3 968 319 discloses a particulate polymer for use in paper coatings, United States Patent 4 196 253 discloses a paper coated with a binder and organic particles, United states Patent 4 371 582 discloses an ink jet recording sheet containing a basic latex polymer, 4 442 247 discloses a coating composition comprising a combination of an aqueous resin with an insoluble resin, United States Patent 4 686 118 discloses a recording medium wherein the coating comprises a combination of a hydrophilic and a hydrophobic polymer, United States Patent 5 102 731 discloses a recording medium wherein the coated layer comprises a hydrophilic urethane resin and fine organic or inorganic particles, United States Patent 5 254 403 discloses a coated recording sheet wherein the receiving layer comprises a mixture of a latex polymer with two hydrophilic polymeric binders, United States Patent 5 270 103 discloses a receiver sheet coated with a coating comprising a pigment,

a binder, and a latex polymer, United States Patent 5 405 678 discloses a coating comprising a latex polymer which has not been completely coalesced, United States Patent 5 672 392 discloses a process for preparing ink jet recording materials whereof the coatings comprise starch, an insoluble copolymer, and a binder, United States Patent 5 714 235 discloses an ink jet recording sheet containing casein and a styrene-butadiene rubber, United States Patent 5 925 712 discloses a fusible printable coating wherein one of the alternative compositions comprises a combination of a powdered thermoplastic polymer and a binder, and Japanese Patent Applications 59/204591 and 59/204592 disclose ink jet receiving coatings which comprise microcapsules which are ruptured after printing to improve the robustness of the image. However the method of this invention is novel and the coatings are particularly suitable for the method.

The following Examples will serve to illustrate the invention:-

Example 1

A formulation was prepared using the following components:-

| | |
|---|---|
| Poly (vinyl alcohol) 10% solution | 40.0g |
| Silicone surfactant | 0.2g |
| Ethylene acrylic acid copolymer beads | 25.0g |
| Optical Brightening Agent | 0.2g |
| Deionised water | 34.6g |

This formulation was coated on to a subbed poly (vinyl chloride) substrate to give a coating weight of 25gm$^{-2}$. An image was printed with pigmented inks using a Novajet III printer, and the coating was passed through a GBC 1200 laminator at a heat setting corresponding to a temperature of 120° together with a piece of paper to seal the image. The paper was removed leaving a smooth clear glossy image which was resistant to wet rubbing.

CLAIMS :-

1. A printing method which comprises the steps of:-

1) Printing on to a receiving material which comprises on a substrate at least one ink receiving layer which comprises particulate polymeric beads which are characterised by a film forming temperature of between 100° and 120° together with at least one hydrophilic binder, and

2) Subsequently heating and applying pressure to the printed image to fuse the polymeric beads.

2. A method according to claim 1 wherein the image is heated using a laminator.

3. A method according to claim 2 wherein the image is heated in contact with an inert sheet.

4. A method according to any one of claims 1,2 or 3 wherein the substrate comprises paper, high wet-strength paper, tracing paper, heavyweight paper, card, board, resin coated paper, polyethylene coated paper, transparency materials, synthetic papers, canvas, cloth, fabric, cellulose acetate, poly(ethylene), poly(propylene), poly (vinyl chloride), poly (ethylene terephthalate) or poly (ethylene naphthalate).

5. A method according to any one of claims 1,2,3, or 4 wherein the binder is poly (vinyl alcohol), tragacanth gum, casein, starch, hydroxyethyl cellulose, carboxymethyl cellulose, poly (vinyl pyrrolidone), gelatin, or a mixture of two or more of these binders.

6. A method according to any one of claims 1,2,3, or 4 wherein the binder is poly (vinyl alcohol).

7. A method according to any one of claims 1,2,3, or 4 wherein the binder is gelatin.

8. A method according to any one of claims 1 - 7 wherein the particulate polymer is polyethylene.

9. A method according to any one of claims 1 - 7 wherein the particulate polymer is a copolymer of ethylene with an acrylate.

10. A method according to any one of claims 1 - 7 wherein the particulate polymer comprises low density polyethylene spherical beads having an average diameter of about 12 μm.

11. A method according to any one of claims 1 - 7 wherein the particulate polymer comprises spherical beads of a 7% acrylic acid/ polyethylene copolymer having an average diameter of about 10 μm.

12. A security printing method according to any of claims 1 - 9 wherein a security mark is embossed on the image at the heating stage.

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## ABSTRACT


### Printing Process

A printing method is provided which comprises the steps of:-

1) Printing with at least one aqueous ink on to a receiving material which comprises on a suitable substrate at least one ink receiving layer which comprises a particulate polymer which is characterised by a film forming temperature of between 100° and 120° together with at least one hydrophilic binder, and

2) Subsequently heating and applying pressure to the printed image to fuse the polymer.

Preferably the printed image is heated by passing through a laminator. Alternatively the printed image is heated by passing through a laminator in conjunction with a second, inert releasing sheet which is held against the top surface of the print material. The second sheet may be used to produce a particular appearance to the final image such as high gloss or a security pattern. The receiving layers of the invention provide bright images after printing and fusing which show a high level of scratch and rub resistance even when wet.